

ON THE RAMAN SPECTRUM OF DIPHENYLMETHANE

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Plate I

ABSTRACT. The Raman spectrum of diphenylmethane has been studied by using λ 4358 as the exciting line, the substance has yielded 18 Raman lines, some of them being not recorded before. These lines are at 3057(6), 2914(3), 2789(4), 1610(6), 1590(4), 1425(2), 1280(2), 1180(2)bd, 1026(6), 1004(10), 813(4)diff., 740(4), 612(4), 550(2), 461(1), 280(2), 231(4) and 194(4) cm^{-1} respectively. The observed frequencies have been compared with those of diphenyl observed by previous authors, and it has been found that all the frequencies of diphenyl are also present in diphenylmethane.

INTRODUCTION

Elizabeth and Grigler (1932) were the first investigators who made an attempt to obtain the Raman spectra of diphenylmethane. They have reported that the lines in the Raman spectrum of diphenylmethane are characteristic of both aromatic and aliphatic linkages. Later, Donzelot and Chaix (1935) investigated the Raman spectrum of this substance but their results do not agree with those of the previous workers. The present investigation on diphenylmethane was undertaken after the Raman spectrum of diphenyl was thoroughly studied in this laboratory by one of us (Mukerji and S. Abdul Aziz, 1938). It was, therefore, considered worth while investigating how far the lines observed in diphenylmethane agreed with those of diphenyl as investigated by them. Our investigation not only verifies the frequencies present in diphenyl but clearly demonstrates that all the important vibrations of diphenyl remain intact in diphenylmethane. In addition, in this substance we have obtained the very important characteristic frequency of the methyl group at 2914 cm^{-1} . The remarkable coincidence between the frequencies of diphenyl and of those of diphenylmethane can be seen in the accompanying Table I. The substance, which was liquid at ordinary temperature, was highly fluorescent but by using suitable filters the continuous spectrum was very greatly suppressed, and the back-ground was more or less free from fluorescence. With an exposure period of about 40 hours as many as eighteen lines were recorded.

EXPERIMENTAL

Diphenylmethane obtained from the Research Laboratory of Eastman Kodak Company was further purified by slow distillation in vacuum. The distillate was directly taken into the U-tube. It was then exposed to the light of a 1000-watt high pressure mercury arc lamp, consuming a

current of about three and a half amperes. Exposures of the order of 40 hours were given and Ilford Selochrome plates were used for photographing the spectra. The spectrograms were obtained with a fairly rapid glass spectrograph, having a dispersion of about 21 A.U. per mm in the region $\lambda 4358\text{\AA}$. The plates were measured with an accurate Zeiss Ikon Comparator and the wavelengths were calculated by the usual method.

TABLE I

Raman shifts in wavenumbers for Diphenylmethane along with those of Diphenyl and Methane.

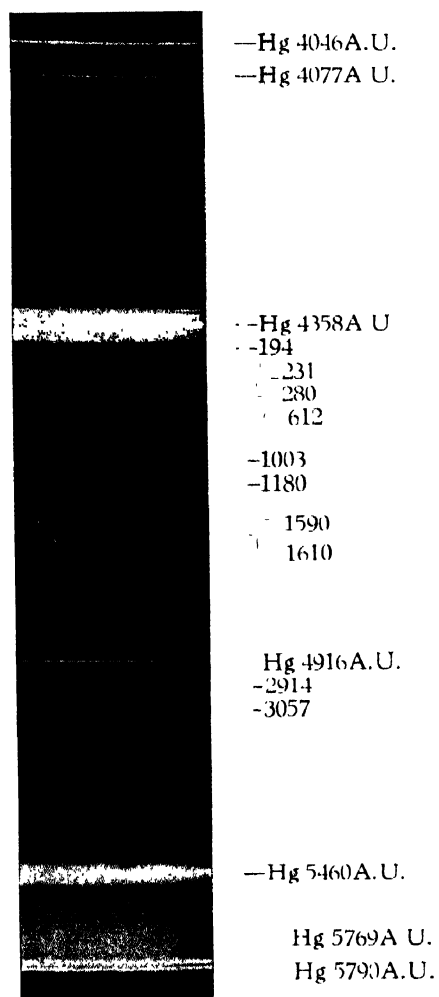
No.	Diphenylmethane.	Diphenyl (Mukerji & Aziz)	Methane
1	194 (4)	193 (0)	
2	231 (4)		
3	280 (2)	267 (4) bd	
4	461 (1)	449 (0)	
5	550 (2)	548 (1)	
6	612 (4) diff	614 (4)	
7	740 (4)	740 (5)	
		779 (4)	
8	813 (4) diff		
		838 (4) bd	
9	1003 (10)	1003 (10)	
10	1026 (6)	1032 (5)	
11	1180 (4) bd	1189 (3)	
12	1280 (2)	1283 (10)	
13	1425 (2)		
14	1590 (4)	1590 (8)	
15	1610 (6)	1610 (10)	
16	2789 (4)		
17	2914 (3)		2914 (10)
			3022 (2)
18	3057 (6) db	3062 (5)	3071 (1)

bd=broad and diffused

d=diffused.

RESULT AND DISCUSSION

Diphenylmethane which was obtained by replacing two of the hydrogen atoms of methane by phenyl groups, was expected to give the fundamental frequencies of benzene which were also found to be present in diphenyl, (Mukerji and Aziz, 1938). As the table given here will show all the seven Raman active modes of vibration of benzene which are considered to be fundamental modes of vibration, have been observed to be present in diphenylmethane. The characteristic frequency of methane at 2914 cm^{-1} is, as the above table will show, was also observed in diphenylmethane. Amongst the other most important frequencies of diphenyl, viz., frequencies at 1610, 1590 and 1003 cm^{-1} respectively observed in diphenyl, have also been found to exist fairly strongly in diphenylmethane. The line at 1178



Raman spectrum of diphenylmethane

cm^{-1} of benzene is also given by this substance on Plate I as a broad and diffused band at 1180 cm^{-1} . But the most intense line of diphenyl at 1283 cm^{-1} , which is not present in benzene, and which appears equally strong in all the compounds of diphenylbenzene family, appears only feebly in diphenylmethane. This shows that the line at 1283 cm^{-1} observed in diphenylmethane has a different origin from that of 1283 cm^{-1} observed in diphenyl and other compounds of the diphenylbenzene family. (Mukerji and L. Singh, 1942, 1945).

Three very low frequency lines, have also been observed in diphenylmethane at 280, 231 and 194 cm^{-1} respectively. The frequency at 231 cm^{-1} which is found to be fairly strong, does not appear in diphenyl. But the very low frequency at 194 cm^{-1} which appears fairly strongly in this substance, appears only as a very feeble line in diphenyl. These low frequency lines are evidently due to lattice oscillations which appear only feebly in diphenyl but are remarkably prominent in diphenylmethane.

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